Studies on the Sintering of the Metallic Powder of the Iron Family. III : On the Sintering of Cast Iron Powder

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Synopsis

Cast iron is easily pulverized with a stamp mill. When heated, the molded powder does not shrink but expands according to the elevation of the heating temperature and is not easily solidified.

The object of this study is to trace various phenomena appearing in the sintering process of cast iron powder, to clarify the cause of expansion, to remove the cause and to make possible the sintering of cast iron powder or cast iron dust powder.

I. Preparation of the Powder and the Sample

The powder was prepared by pulverizing cast iron with a stamp mill, the composition of which is shown in Table 1. For convenience, some of the samples for the measurement of expansion (or shrinkage) and electric resistance were prepared by mixing cast iron powder with soft iron powder, which was a commercial product containing less than 0.1 per cent carbon and of the fineness of minus 150 mesh.

Table 1

Composition	T.C.	Si	P	S
%	2.97	3.31	0.27	0.05

The above powder was molded with pressure of a few ton/cm^2 and then sintered. The treatment was conducted in the atmosphere of hydrogen or graphite powder. The hydrogen was introduced into the sintering furnace from a cylinder after passing through heated copper, a saturated solution of potassium hydroxide, calcium chloride and phosphorous pentoxide. In the case of carbonsintering, graphite was loosely charged in a silicate tube, in which the sample was buried. The both ends were lightly covered with asbestos and the tube was heated.

II. The Experimental Results and the Discussion

(1) The change of expansion by mixing with soft iron powder

The expansion of a mixture of cast iron powder and soft iron powder at each sintering temperature was first examined. The mixture was molded in a rod of $6\times6\times150$ mm and sintered in hydrogen or graphite atmosphere. The preparation of each sample is shown in Table 2. The expansion rate was determined by

measuring the change of the length between two marks about 5 cm apart marked by a knife edge on the sample; it showed a linear expansion rate in a right angle direction to the compressing force. The relation between the expansion rate and temperature obtained by measuring the same sample keeping at each temperature for 1 hour, is shown in Fig. 1. The density after the sintering is shown in Table 2. Fig. 1-A shows the case of hydrogen-sintering and B the graphite-sintering. Below 500°C, no change was observed in each case, but above 500°C, each sample expanded. In both sintering cases, the expansion rate was great so long as the content of cast iron powder was large and the molding pressure was strong. But the former effect was greater then that of the latter. The compact of cast iron powder only expanded too much and sometimes the sample cracked, which made

Table 2. Preparation of the sample

Nos.	C. I. (%)	Fe (%)	Molding pressure (ton/cm^2)	Atmosphere	Density after the sintering
7	30	70	5	Hydrogen	5.3
8	50	50	5	"	5.1
9	70	30	5	"	4.8
12	30	70	7	"	5.2
13	50	50	7	"	4.9
14	70	30	7	"	4.6
22	30	70	5	Graphite	5.3
23	50	50	5	"	4.6
24	70	30	5	"	4.8
27	30	70	7	"	5.4
28	50	50	7	"	4.8
29	70	30	7	"	4.7

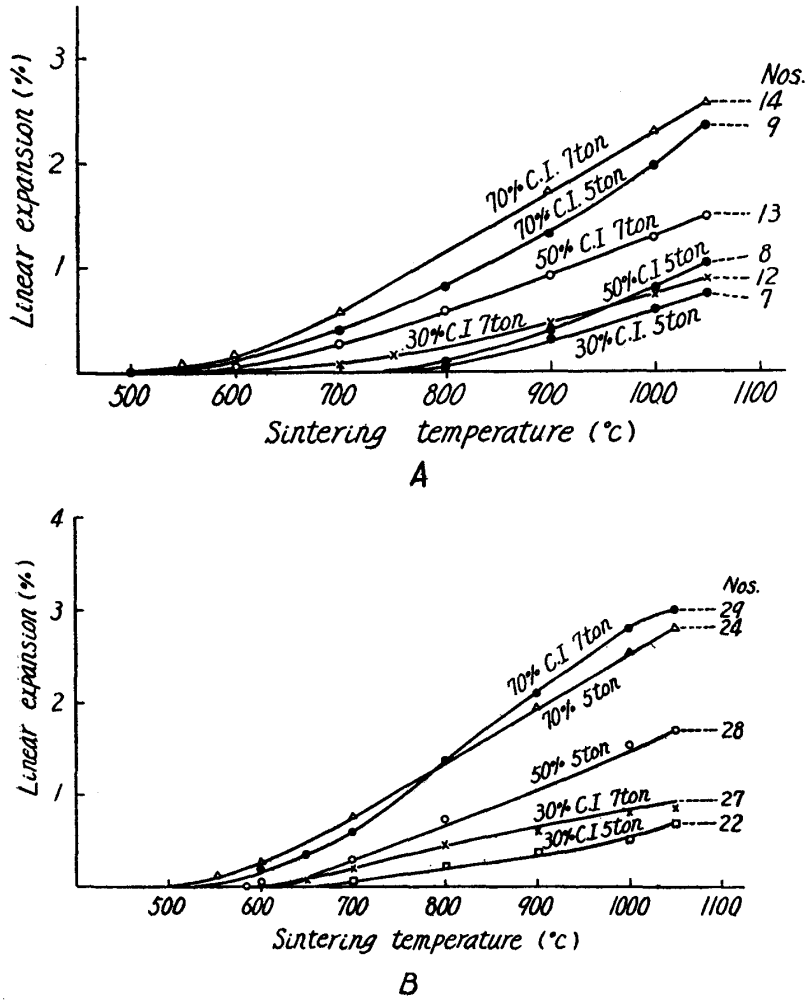

Fig. 1. Effect of sintering temperature on expansion.
A, sintered in hydrogen atmosphere.
B, in graphite powder.

the measurement difficult, so that soft iron powder was mixed. Generally, when the compressing force was too great, metal powder compact was expanded by a gas in the case of sintering. In the present case, the density after molding was 5.0~6.0. And as cast iron powder was hard and difficult to cause plastic deformation, there would be an escaping of gas under the pressure given here. As seen from the figure, the fact that the effect of the amount of cast iron was larger than that of the other showed that the expansion by sintering was the substantial phenomenon of the cast iron. Almost no effect of atmosphere on the expansion rate was found. The cause of expansion must be due first to the growth of cast iron as seen in massive cast iron and then to the oxidation of silicon in cast iron. The consideration on these causes will be given after the measurement of resistance, because the change of resistance appears more sharply at some times.

(2) The change of electric resistance

At the same time with measurement of the expansion rate, the specific resistance of each sample was measured using a potentiometer, and the result is shown in Fig. 2. Fig. 2-A shows the case of hydrogen sintering and 2-B the carbon sintering. A sample containing 50 per cent soft iron powder was molded with 6.6 ton/cm^2 pressure and its specific resistance was continuously measured

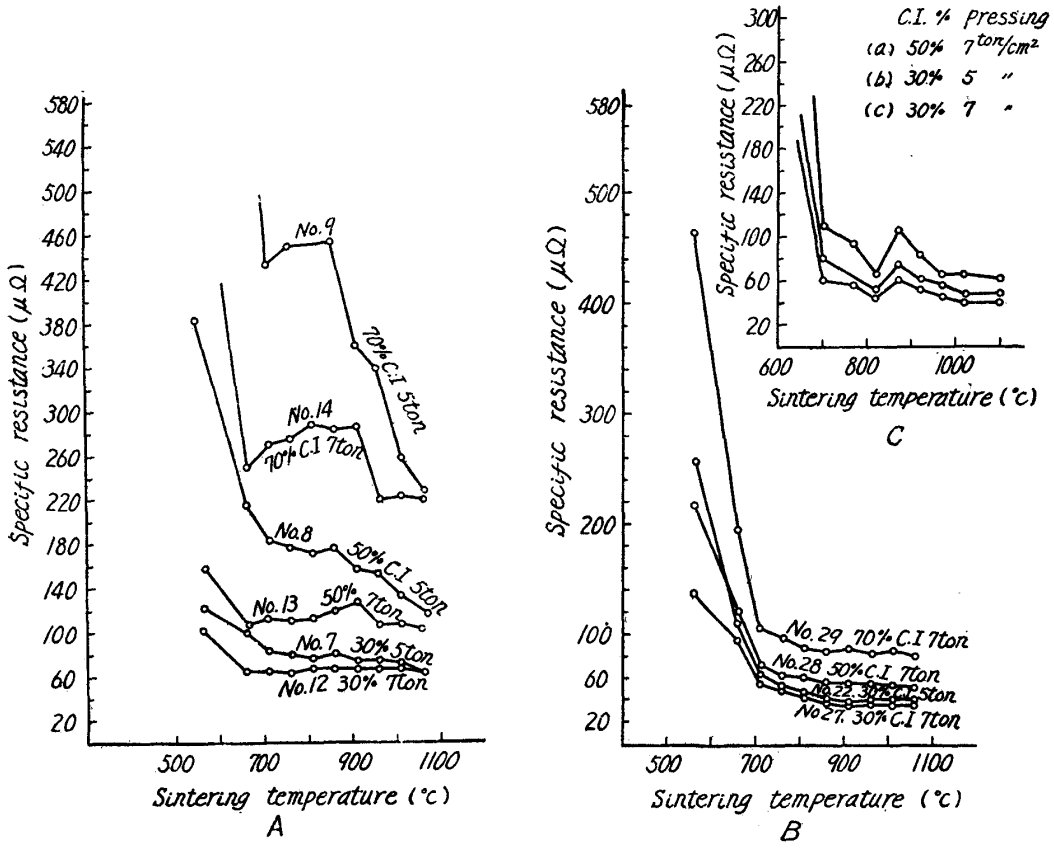

Fig. 2. Effect of sintering temperature on specific resistance.
A shows the case of repeated sintering in hydrogen, B, the case of repeated sintering in graphite powder and C, the case of sintering in graphite powder.

while heating in hydrogen and its result is shown in Fig. 3. As the powder had not been reduced previously, its surface was very dirty and its contact resistance after molding was very great, reaching a few thousand micro ohms. With the elevation of the sintering temperature, volatile component fixed on the surface of the powder evaporated off and oxides on the surface was reduced, and the specific resistance quickly decreased. When sintered in hydrogen, the specific resistance quickly decreased, but it increased above 700°C and attained the maximum value at 800~900°C. This tendency hardly appeared when the amount of cast iron was small, but it appeared distinctly when the amount of cast iron was more than 50 per cent. Also in I-curve in Fig. 3, the similar tendency was perceived. Ordinarily, in cast iron the structure change occurs above 700°C and the whole volume expands. The peak of the resistance should be considered in connection with this phenomenon. Here, it should be noticed that as the solidification of the compact did not yet occur as seen from Fig. 1, the high resistance shown by Fig 2-A was not the resistance of cast iron itself, but was mainly due to its contact resistance. As cast iron is very hard and hardly causes plastic deformation, the specific resistance of the compact generally becomes great. And before being compact, the structure change due to the dissolution of cementite occurs, and the uneven expansion will occur in the inner part of the compact, causing an increase in the contact resistance.

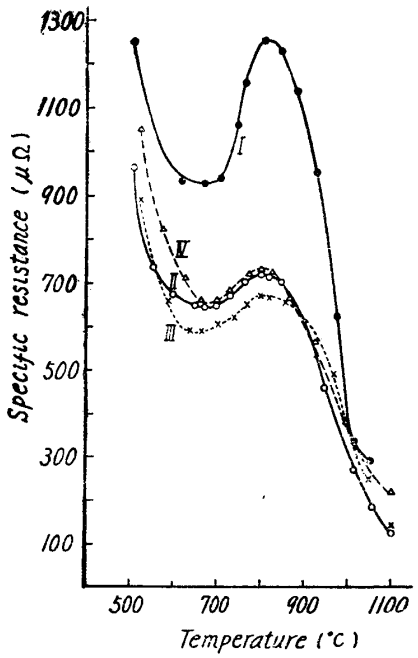

Fig. 3. Continuous measurements of specific resistance. The compacts consist of 50 per cent C.I. powder and res iron. Annealing temperatures of C.I. powder; (I) non annealed (II) 700°C, (III) 800°C, (IV) 900°C.

But the above phenomenon is different of occurrence in the carbon-sintering. In the repeated experiments in the carbon sintering, the peak hardly appeared and the last value of resistance was very small compared with that in the hydrogen sintering. In a single experiment in the carbon sintering, a peak slightly appeared as shown in Fig. 2-C, but it was small. In a discussion of such a phenomenon, the atmosphere in the carbon sintering should be taken into consideration. At very low temperature, the atmosphere is air. At the stage where the reaction between graphite and oxygen took place, carbon monoxide or dioxide was produced and the equilibrium along Boudouard curve was maintained. But, at low temperature, as carbon dioxide dominated in the space, the atmosphere at low temperature sintering was oxidizing one. In the case of Fe-C-O ternary system the cementite was decarburated. As this action proceeds from the surface of the powder, the interior of the grain may be composed of Fe_3C, but the surface structure will be rich in α-Fe and the atom movement is easily promoted

in accordance with the elevation of temperature, and the contact resistance decreases, that is a net combination is formed in the inner part of the compact, by which the specific resistance is decreased. But when the repeated experiment is not conducted, decarburization hardly occurs even in the carbon-sintering. In this way, the peak shown in Fig. 2 C was produced.

(3) The cause and the prevention of the expansion of cast iron powder

The result of the continuous measurement of the expansion rate is shown in Fig. 5 and the apparatus using for the purpose in Fig. 4. In Fig. 4, A is a silicate tube of 30 mm ϕ, on the bottom of which sample S is placed and then a thin copper plate on S, and a thin silicate tube B stands on the copper plate. A dial gauge D is attached to B and fixed. The lower half of A is put in a furnace and heated in the current of hydrogen and the expansion rate is read by dial gauge D. S was cast iron powder and molded to a rod of 17.5 mm ϕ $\times$ 20 mm l with the pressure of 5 ton/cm^2, the density of which was about 4.9. The curve-I shows the case at 7°C/min. At low temperature, it expanded slightly through thermal expansion. The expansion rate became larger at about 500°C and reached the end at 950°C. There was a turning point at 720°C, but the cause of the formation of the point was not clear. When the elevating temperature was 3°C/min., the rate followed almost the same course. Fig. 5 is not perfectly coincidental with Fig. 1. The difference between the continuous measurement and the repeated experiment was also perceived in the measurement of resistance. In the repeated experiment, an accurate result was not obtained because of many factors. The domain of the steep elevation of the curve in Fig. 5 was at 600~800°C, which was the same as that of the specific resistance. The cause of such expansion was to be found in the structure change according to the elimination of cementite. The curve-II shows the case of annealing of the powder in the current of hydrogen at 700°C for 2 hours, in which the slow expansion began at about 500°C at the former case was eliminated and the expansion rate became small throughout the whole course. The curves II~IV in Fig. 3 show the change of specific

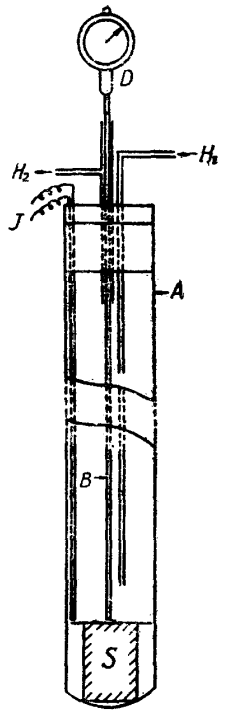

Fig. 4. Schematic apparatus for continuous measurements of expansion.

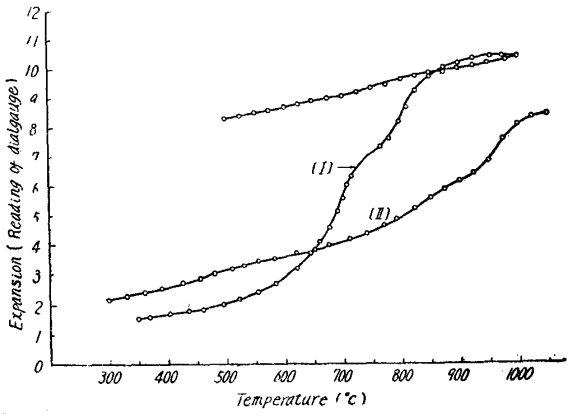

Fig. 5. The results of continuous measurements of expansion. Treatment of powder, (I) non (II) annealed.

resistance in the case of annealing of cast iron powder, and their heights were by far lower compared with the peak of the curve I. When cast iron was pulverized, each grain was not necessarily made of the same constitution, and free cementite particle would be contained in it. The expansion beginning at 500°C and seen in the curve-I in Fig. 5 must have been due to graphitizing of such free cementite or to the oxidation of silicon in the cast iron, and to determine it is difficult at present. Silicon oxide cannot be reduced by hydrogen but silicon is oxidized with a trace of oxygen in hydrogen, by which the compact will expand.(1) As the free cementite is easily graphitized, the effect can be removed by the annealing of the powder. In the case of silicon, if it is oxidized at the same time with the annealing, the expansion of the compact at low temperature can be prevented. At any rate, the expansion could be prevented to a certain degree by the annealing of the powder. When a powder anneald at 800°C was used, it fairly expanded below 1,000°C, in both carbon and hydrogen sinterings as shown in Fig. 6. At higher temperature, it continued to expand in the carbon sintering, but its shrinkage began to occur in hydrogen, which must have been due to the commencement of mutual combination of particles due to the distinct decarburization by hydrogen. But its sintering temperature reached almost 1,100°C and such an operation almost at the melting point was not practicable and required another means. For comparison, the results obtained by using the soft iron powder and the mixture of the cast iron and the soft iron powders are shown in Fig. 6. From the above consideration, it is supposed that if the cementite is perfectly changed into graphite, the expansion would not occur. But for the purpose, the treatment should be conducted at high temperature for a long time, which is also not practicable. The cast iron powder, annealed at 900~1,000°C for 12 hours in hydrogen, caused further expansion. Generally, the annealing at such high temperature and for a long time should be avoided as it gives bad effect on the sintering property of the powder. To avoid expansion by decarburization of the powder is assumed from the example of the carbon-sintering shown in Fig. 2. But, to decarburize the powder in hydrogen requires long hours' treatment at

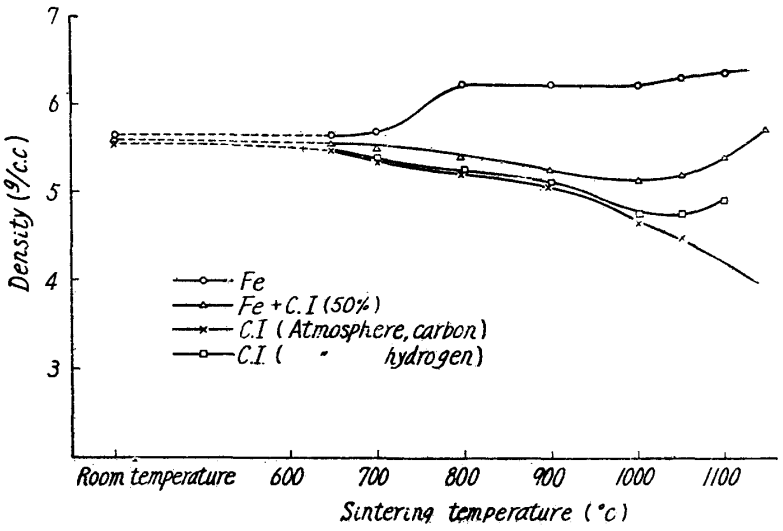

Fig. 6. Relations between density and sintering temperature of iron and cast iron powder compacts.

(1) The same example is seen in an alloy containing aluminium. See part IV of this studies.

high temperature, and so the powder previously roasted in the air and then reduced with hydrogen was used.

(4) On the effect of decarburization

By annealing above 500°C in air the cast iron powder was quickly decarburized. When annealed at 500~700°C for 30~60 minutes, various powders having different degrees of decarburization were obtained. As the powder was slightly solidified, it was ground in a mortar, reduced in hydrogen at 650~700°C for 3 hours and used in the experiment. Three kinds of powder were used and their carbon contents are shown in Table 3. These three powders were molded into rods of 17.5 mm ϕ × 17 mm l and the relations between temperature and shrinkage are shown in Fig. 7, being the results of repeated experiments with each sample. The sintering was conducted in the current of hydrogen for 1 hour. C powder having low percentage of carbon did not expand and its shrinkage was fairly great. A turning point was perceived at 950°C, which must have been due to the transformation.

Table 3. Carbon content of decarburized powders

Powder	Carbon content (%)
A	1.08
C	0.88
D	1.96

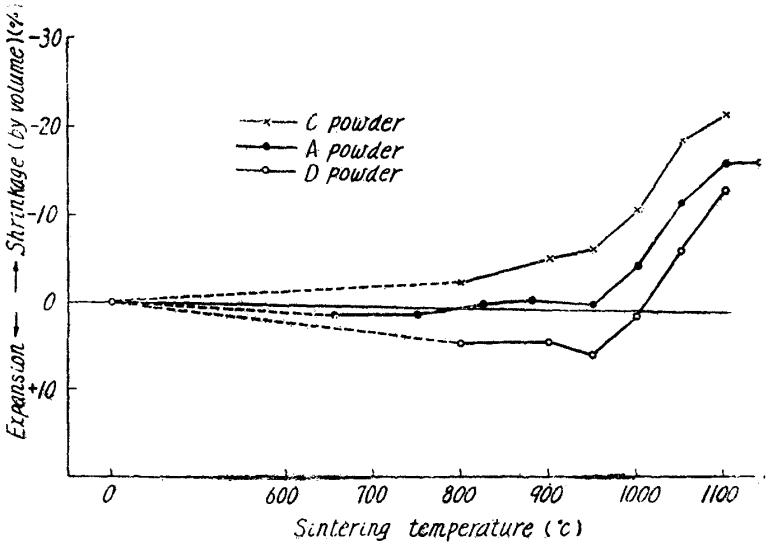

Fig. 7. Relations between volume change and sintering temperature of decarburized powders.

Samples containing larger amounts of carbon expanded at 600~700°C, which was due to the decomposition of the residual cementite. At further elevation of temperature, it shrank, expanded again through the transformation at 950°C and then shrank at higher temperature. The larger the carbon content was, the greater the expansion rate. As seen from Table 4, even with the same molding pressure, the density differed according to the kind of the powder, and the density after molding was greater when the carbon content was larger.

Table 4. Density of A, C and D powder compacts

Sample No.	Powder	Molding pressure (ton/cm^2)	Density	
			After molding	After sintering at 1,100°C
015	A	5	4.7	5.44
121	C	5	4.2	4.85
122	D	5	5.0	4.7

The above fact must have been due to the action of the residual graphite as a lubricant and to the increase of the surface resistance to the pressure owing to larger lattice vacancy of the surface by the reduction of greatly oxidized powder. The powder containing large amounts of carbon attained great density after molding, but did not gain the maximum density after sintering, because the expansion rate at the sintering became great. Observing both the effects, for getting the maximum density after the sintering, *A*-powder containing about 1 per cent carbon will be the best.

But it is difficult to reduce perfectly these powders, and the remaining oxygen reacts with carbon in the course of sintering, so the carbon content after the sintering decreases. For example, the carbon content of the sintered product of *A*-powder was about 0.5 per cent.

The change of shrinkage due to the difference of density will be explained later; it is, however, smaller than the difference due to the carbon content in the above domain of pressure.

As stated above, the expansion was prevented by the decarburization. In the change of electric resistance shown in Fig. 2-B, in the case of the repeated experiment for sintering in graphite, the peak hardly appeared at 800°C, which may be explained as the effect of decarburization. In other words, in the case of the carbon sintering at low temperature, the sample was oxidized, as the partial pressure of carbon monoxide was very low. The mechanical properties of the sintered product obtained by using these three kinds of powder are shown in Table 5 and in Fig. 8. The samples were molded into rods of 6×6×150 mm and sintered in hydrogen. The tensile strength became great with the progress of sintering, which was due to the combined result of the increase in the cohesion of the particles and of the density. It should be noticed that the sample attained the tensile strength almost equivalent to that of an ordinary cast iron at low density such as 5.4~5.5. But the elongation was very small, at least, about 1 per cent.

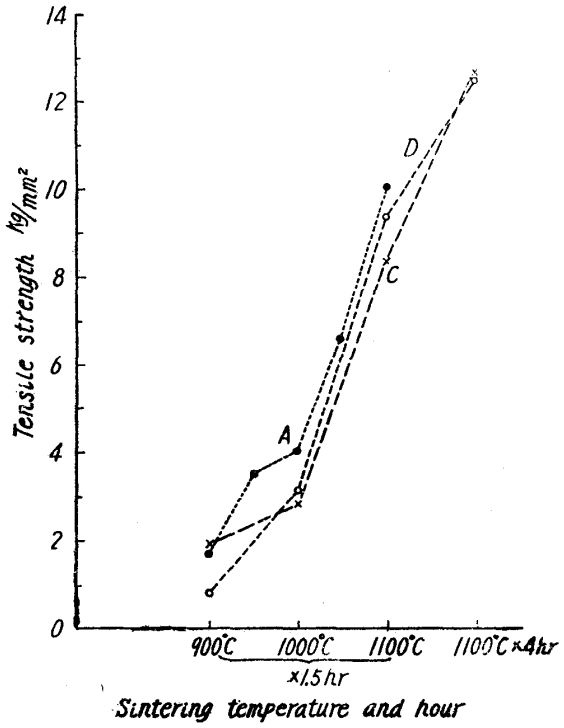

Fig. 8. Relations between tensile strength and sintering conditions of decarburized powders.

(5) On the anisotropy of the expansion of the compact

In the former section, the outline of the sintering process of the decarburized powder was given. It was seen that the expansion rate was different according to the direction in case of the expansion of the powder. When the compressing

Table 5. Mechanical properties of the sintered compacts of A, C and D powder

Sample No.	104	105	106	107	108	109	155	157	161	163	156	158	162	164
Powder	A	A	A	A	A	A	C	C	C	C	D	D	D	D
Sintering-temperature (°C)	900	950	1000	1050	1100	1100	900	1000	1100	1100 4 hrs.	900	1000	1100	1100 4 hrs.
Density after sintering	4.6	4.7	4.7	4.8	5.1	5.3	4.3	4.4	5.0	5.4	4.9	4.8	5.1	5.5
Tensile strength (kg/mm²)	1.7	3.5	4.6	6.0	10.1	13.3	1.9	2.7	8.3	12.6	0.8	3.1	9.2	12.5

* Repressed by the pressure 5ton/mm² and then resintered.

direction is denoted as L and the vertical direction to L as ϕ, the expansion rate in the L direction is very great. The result for the sample shown in Table 4 is shown in Fig. 9. The tendency was about the same for each powder. The phenomenon must be a general one appearing in the expansion of the compact, but it is not caused by the powder itself. No anisotropy was seen in the case of shrinkage.

(6) On the effect of the pressure

The relation between the molding pressure and the density of *A*-powder are shown in Fig. 10. The sintering was conducted in the current of hydrogen. The density of the compact after the molding linearly changed in a certain limit and its shrinkage was large

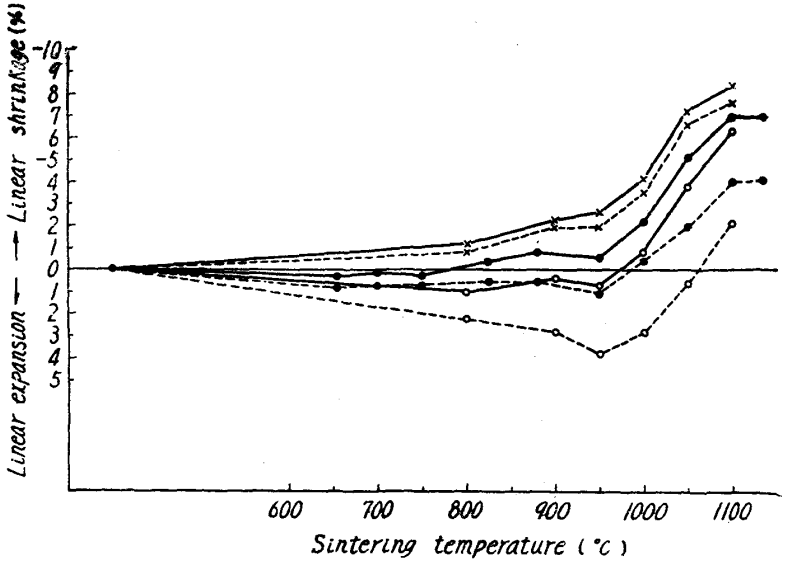

Fig. 9. Anisotropy of schrinkage

	Powder	Direction
---×---	C	Parallel to pressing line
—×—	C	Normal to " "
---•---	A	Parallel to " "
—•—	A	Normal to " "
---○---	D	Parallel to " "
—○—	D	Normal to " "

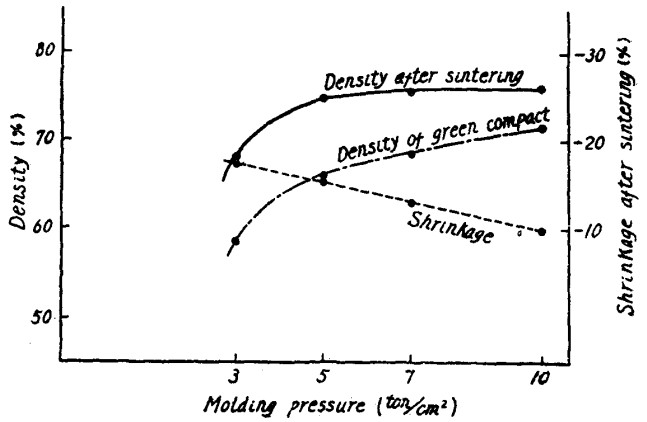

Fig. 10. Effect of molding pressure on density and shrinkage.

when the molding pressure was small, so the change of the density after the sintering at 1,130°C was comparatively small and in a linear relation.

Conclusion

(1) By observing the various phenomena in the sintering process of cast iron powder, it was made clear that the main cause for the great expansion rate and the formation of peak in the resistance was the oversaturation of carbon.

(2) By removing the oversaturated carbon, the expansion could be lessened in the degree not to hinder the sintering.

(3) By annealing the powder, the expansion rate of the compact was lessened and it was solidified in hydrogen above 1,050°C, but not in graphite.

(4) For removing the oversaturated carbon, decarburization by roasting was simple and effective.

(5) The compact of decarburized powder shrank at 1,000°C in the case of large amounts of carbon, but at 800°C when the carbon content was small, and the rate of shrinkage was fairly great.

(6) As one of the mechanical properties, the tensile strength was measured. In the case of the decarburized powder, its tensile strength developed with the progress of the sintering and corresponded to that of an ordinary cast iron at the density of about 70 per cent. But elongation was almost zero.

(7) In the expansion process, the rate was different in the parallel and vertical directions to the pressing directions, but the same phenomenon was not observed in the shrinkage.

(8) By examining the relation between the molding pressure and the density, a pressure domain was found, in which the density after the sintering changed in a linear relation.